THE IDENTIFICATION OF OLEFINS AS THIOCYANATES

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By

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INTRODUCTION

At present, the identification of low boiling unsaturated hydrocarbons which yield only liquid addition products with the halogens and hydrogen halides is often a matter of considerable difficulty. This fact is sufficient reason for the study here described. In some cases, especially among terpenes, the compounds formed by adding NOCl, N_2O_3, or N_2O_4 at one or more of the double bonds have been used as derivatives but these are inconvenient to make, of uncertain composition, and decidedly unstable. This work consists of (1) attempts to find a convenient samll scale method for adding $(SCN)_2$ to olefins, (2) the determinations of the melting points of the derivatives, and (3) quantitative analysis of derivatives to prove their structure and purity.

HISTORICAL

Liebig (1) first attempted to prepare free thiocyanogen shortly after the discovery of the first halogenoid, cyanogen. Much investigation followed but Söderbäck (2) was the first actually to isolate the free radical in 1920, the long delay being due, probably, to the lack of stability of this compound.

Söderbäck first obtained free thiocyanogen by the action of iodine on an ethereal suspension of silver thiocyanate. He later showed that bromine gave a more nearly complete reaction and that the character of the product was influenced by the solvent, the concentration, and the local heat effects. Other early methods of preparation are the oxidation of thiocyanic acid either in ethereal solution by manganese dioxide, or by its interaction with lead tetraacetate (3), and the electrolysis of thiocyanates (4).

Kaufmann and Küchler (5) have found that black cupric thiocyanate, with or without the help of a reducing agent, can be converted into white cuprous thiocyanate. Their method at first employed precipitated and dried cupric thiocyanate. They, however, found this separate preparation unnecessary and used instead a mixture of copper sulfate and inorganic thiocyanate. If water of hydration is present the reaction converting alkali thiocyanate to cupric thiocyanate occurs merely by rubbing the reagents together. If, for example, copper sulfate is intimately mixed with sodium thiocyanate, there is formed a black paste of cupric thio-

cyanate and sodium sulfate.

Kaufmann (6) has shown that the tendency of thiocyanogen to polymerize is less in glacial acetic acid than in any other solvent. He also points out that contact with moisture or with air lessens the stability.

Gardner, Priblyl, and Weinberger (7) state that with unsaturated members of the C_nH_{2n} series, thiocyanogen forms addition products:

$$R\text{-}CH{=}CH\text{-}R + (SCN)_2 \rightarrow RCH(SCN)CH(SCN)R$$

With olefinic members of the C_nH_n series (diolefins) it is added at only one of the double bonds, while with compounds containing a triple bond there is no addition. The latter is probably in error in view of the results published by Söderbäck (8).

Kaufmann (9) applied solutions of thiocyanogen, or nascent thiocyanogen, in suitable media in the preparation of ethylene dithiocyanate, m. 90°, styrene dithiocyanate, m. 101°-102°, allyl alcohol dithiocyanate, an oil decomposing on distillation, anethole dithiocyanate, m. 87°, and isosafrole dithiocyanate, m. 109°. His experiments show that free thiocyanogen unites with unsaturated compounds but with less energy than bromine, occupying in this respect a position between bromine and iodine.

Söderbäck (8) finds ethylene dithiocyanate results in nearly theoretical yields from thiocyanogen and ethylene in benzene; anhydrous ether gives poor yields, due to the formation of thiocyanic acid. Styrene dithiocyanate was prepared in 79.5% yield; it crystallizes with one mole of

benzene. Stilbene dithiocyanate was formed in 87% yield, m. 225°-226°. Acetylene and thiocyanogen react only in the presence of light, giving a mixture of the solid trans-acetylene dithiocyanate, m. 97°-98.5°, and the liquid cis-acetylene dithiocyanate, f. 0°, m. 15°-17°. Söderbäck also prepared phenylacetylene dithiocyanate, m. 67°-68°, and α-tolane dithiocyanate, m. 194°-195°. β-Tolane dithiocyanate, m. 123°-124°, was prepared from the dibromide and thiocyanogen.

Kaufmann and Oehring (10) obtained ethylene dithiocyanate, m. 90°, by passing chlorine and excess ethylene into a cold suspension of sodium thiocyanate in acetic acid. They also obtained styrene dithiocyanate, m. 101°, and anethole dithiocyanate, m. 87°, by treatment of the olefins with bromine and sodium thiocyanate in acetic acid.

Bruson and Calvert (11) studied the reaction of thiocyanogen, made from potassium or sodium thiocyanate and bromine in acetic acid, with isoprene and methyl isoprene and obtained good yields of crystalline dithiocyanates, m. 76°-77° and 130° respectively, suitable for identifying the olefins. In contrast to the method of Söderbäck who allowed his reactions to proceed in strong sunlight, these investigators prepared their compounds in a darkened room. Bruson and Calvert are the only authors who have mentioned using thiocyanates in qualitative organic analysis.

Krassilchik (12) states some hydrocarbons, e. g. stilbene, do not react with thiocyanogen. This recent work is obviously in contradiction to results given by Söderbäck

(8) and cited above.

Muller and Freytag (13) passed butadiene into an ether solution of thiocyanogen and obtained a good yield of 1,4-dithiocyanobutene-2, m. 83.5°.

EXPERIMENTAL

The chemicals used are listed on the following pages with an indication of their source and purity.

OLEFINS

Ethene	-Ohio Chemical and Manufacturing Company
Propene	-Made by the author. 100 ml. of isopropyl alcohol and 150 ml. of 75% sulfuric acid were heated in the presence of 10 grams of infusorial earth. The propene was freed from acetone by washing in a solution of sodium bisulfite as it was generated.
1,3-Dibromopropane (Trimethylene Bromide)	-Eastman Kodak Company product. b. 165°-167°
Allyl Alcohol	-Eastman Kodak Company product. b. 97°
Allyl Bromide	-Eastman Kodak Company product. b. 71°-72°
Butene-1	-Made by the author. 1,3-Dibromobutane was dissolved in three times its weight of alcohol and three its weight of powdered zinc added. The mixture was refluxed and the olefin used as generated.
2,3-Dibromobutane	-Eastman Kodak Company product. b. 155°-157°

1,2-Dibromo-2-methyl-propane (Iso-butene Dibromide)	-Eastman Kodak Company product. b. 36°-37° /10 mm.
Pentene-2	-Eastman Kodak Company product. b. 35°-37°
1-Methyl butene-2 (Trimethylethylene)	-Eastman Kodak Company product. b. 36°-38°
Methyl Isoprene	-Chem. 620, student preparation by dehydration of pinacol. b. 69.5°-70° /350 mm.
Octene-2 (Caprylene)	-Eastman Kodak Company product. b. 124°-126°
1,6-Dimethylhexene-3 (Di-isobutene)	-Eastman Kodak Company product. b. 101°-102.5°
Styrene	-Made by the author. One mole of dry, powdered cinnamic acid and 2 grams of hydroquinone were fractionally distilled and the portion boiling below 125° was collected. This was steam distilled, separated and dried with a small amount of calcium chloride. (16)
d-Limonene	-Eastman Kodak Company product. b. 177°
Cyclohexene	-Eastman Kodak Company product. b. 82.5°-83.5°
3-Methylcyclohexene-1	-Eastman Kodak Company product. b. 100°-101°

Pinene	-Eastman Kodak Company practical product. Purified by the author by fractionating over sodium metal. b. 154°-156°
REAGENTS	
Copper Sulfate	-E. H. Sargent Technical
Sodium Thiocyanate	-Mallinckrodt Pure
Lead Thiocyanate	-Prepared by Dr. Dermer. Calculated amounts of lead nitrate and sodium thiocyanate were mixed in solution and the product filtered off, and washed with water and dried at 110°.
Bromine	-Texaco SaltProducts Co. Technical
Sodium Carbonate	-Wilkens-Anderson. Technical
Zinc	-General Chemical Co. Reagent
SOLVENTS	
Glacial Acetic Acid	-Mallinckrodt. Reagent
Benzene	-E. H. Sargent. Pure. b. 79°-81°
Thiophene-free Benzene	-E. H. Sargent. Reagent. m. 5°
Alcohol	-American Alcohol Corp. 95% b. 78.5°-79°
Ligroin	-Eastman Kodak Co. Practical.
MISCELLANEOUS	
Charcoal	-Industrial Chemical Co. Nuchar.
Supercel	-Johns Manville.

EXPERIMENTAL PROCEDURES

The experimental work of this problem may be divided into three phases:

1. The preparation of the olefin dithiocyanates.
2. Analysis of the compounds to determine composition.
3. Determination of melting points.

The two general methods used here are essentially those of Kaufmann and Küchler (5) (method A) and of Söderbäck (8) (method B) with some modifications. In method A 10 ml. unless otherwise stated, of the olefin was added to a suspension of 64 grams of sodium thiocyanate and 64 grams of copper sulfate, both finely ground, in 150 ml. of glacial acetic acid. This mixture was shaken vigorously, care being taken to keep the mixture cool. After standing for some time the mixture was filtered* and the filtrate added to 500-800 ml. of water. In some instances when the amount of product separating was small the acid was partly neutralized with sodium carbonate. The product was separated by filtering or skimming and dissolved in 50 ml. hot benzene, boneblacked, and filtered. The filtrate was evaporated nearly to dryness and cooled. Ligroin was added and the solid product, if any, filtered off and purified.

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*It was found that by centrifuging the mixture and filtering the supernatent liquid through Supercel, the filtration proceeded more easily and rapidly.

In the second method the olefin was added to a suspension of 20 grams of lead thiocyanate in 100 ml. of thiophene-free benzene to which had been added 8 grams of bromine. The mixture was kept in an ice bath in direct sunlight with frequent shaking for about an hour or until the brown color of the mixture disappeared. The mixture was then filtered and the benzene evaporated on a steam bath. The product was taken up and purified in a suitable solvent.

The composition was determined by analyzing for sulfur or for nitrogen. The sulfur analysis was determined by fusing the sample with sodium peroxide and potassium perchlorate in a bomb and determining the sulfate gravimetrically as barium sulfate (14). Analysis for nitrogen was by the Kjeldahl method.

Melting points were determined by two observers using a large, lighted sulfuric acid bath with motor stirrer and a calibrated thermometer. All melting points are corrected for stem exposure.

ETHENE

Ethene was intermittently bubbled through a solution of thiocyanogen (method B) until the brown color of the mixture disappeared. After filtration and evaporation the residue was dissolved in boiling water and filtered. The ethene dithiocyanate separated in long white crystals. The product was purified by recrystallization from hot water and dried in vacuum at room temperature, m. 90°-90.5°. Because of the close agreement of the melting point with

the literature values, no analysis was made.

$$CH_2{=}CH_2 + (SCN)_2 \rightarrow CH_2(SCN)CH_2(SCN)$$

PROPENE

The propene dithiocyanate was prepared by the (method A) with the usual amount of the salts in 150 ml. of glacial acetic acid. The mixture was treated with propene until it was decolorized and then allowed to stand overnight in the ice box. Upon completing (method A) propene dithiocyanate separated in white crystals which were filtered off and purified by recrystallization from alcohol-water solution and dried in vacuum at room temperature, m. 103°-104°. Analyzed for sulfur. Calculated for $C_3H_6(SCN)_2$; 40.53% S. Found; 41.01% S.

$$CH_3CH{=}CH_2 + (SCN)_2 \rightarrow CH_3CH(SCN)CH_2(SCN)$$

CYCLOPROPANE

Two attempts were made to prepare 1,3-dithiocyano-propane. The first method was the ring cleavage and addition of thiocyanogen; the second was direct metathesis with the dibromide. In the first method the cycloparaffin was generated by refluxing trimethylene dibromide with three times its weight of alcohol and twice its weight of powdered zinc. The hydrocarbon was treated by method B until the brown color of the mixture disappeared. After filtration and evaporation the residue was dissolved in hot alcohol and filtered through Supercel. The filtrate was evaporated to 10 ml., cooled and added to 50 ml. of water. The final product separated as a yellow oil which gave some evidence of crystallizing at about -10°.

In the second method 5 ml. of the trimethylene dibromide was refluxed one hour with a solution of 20 grams of sodium thiocyanate in 30 ml. of ethanol. The mixture was filtered through Supercel and the filtrate evaporated to 10 ml. Water was added and the product separated as a yellow oil.

ALLYL ALCOHOL

Allyl alcohol was treated by method A and allowed to stand overnight in the ice box. Upon completion of method A the allyl alcohol dithiocyanate separated as a brown oil.

ALLYL BROMIDE

Allyl bromide was treated in the same manner as allyl alcohol. The dithiocyanoallyl bromide separated as a yellow oil.

BUTENE-1

As the butene-1 was generated it was allowed to bubble through a solution of thiocyanogen (method B) until the brown color of the mixture disappeared. After filtration and evaporation the residue was dissolved in hot alcohol and filtered through Supercel. The filtrate was evaporated to 10 ml. and water added. The 1,2-dithiocyanobutane separated as a yellow oil.

BUTENE-2

Owing to the failure of the butene-1 to give a solid dithiocyanate, the butene-2 was not tried directly. Instead 5 ml. of 2,3-dibromobutane was refluxed for 30 minutes in a mixture of 20 grams of sodium thiocyanate in 30 ml. of alcohol. The mixture was cooled, filtered through Supercel,

and the filtrate evaporated to 10 ml. Water was added and the 2,3-dithiocyanobutane separated as a yellow oil.

ISO-BUTENE

Following the above procedure, 5 ml. of 1,2-dibromo-2-methylpropane was refluxed for 30 minutes in a mixture of 20 grams of sodium thiocyanate in 30 ml. of alcohol. The mixture was cooled, filtered through Supercel, and the filtrate evaporated to 10 ml. Water was added and the 1,2,-dithiocyano-2-methylpropane separated as a yellow oil.

PENTENE-2

Pentene-2 was added one ml. at a time at five minute intervals to a solution of thiocyanogen (method B) until the brown color of the mixture disappeared. After filtration and evaporation the residue was dissolved in hot alcohol and filtered through Supercel. The filtrate was evaporated to 10 ml. and water added. The 2,3-dithiocyanopentane separated as a yellow oil.

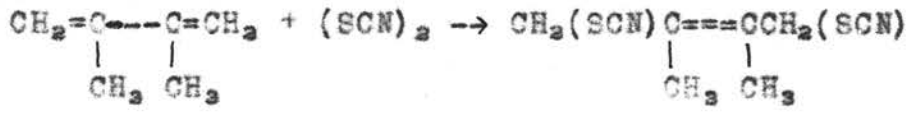
1-METHYLBUTENE-2

1-Methylbutene-2 was added intermittently to a solution of thiocyanogen (method B) until the brown color of the mixture disappeared. After filtration and evaporation the residue was dissolved in hot alcohol and filtered through Supercel. The filtrate was evaporated to 10 ml. and water added. The 1-methyl-2,3-dithiocyanobutane separated as a yellow oil.

METHYL ISOPRENE

Methyl isoprene was treated by method A and allowed to stand overnight in the ice box. Upon completion of

method A a very small amount of 1,4-dithiocyano-2,3-dimethylbutene-2 separated in white crystals which were filtered off, purified by recrystallization from alcohol-water solution and dried in vacuum at room temperature, m. 130.5°-131°. An insufficient amount of the product was obtained to make a chemical analysis.



OCTENE-2

The 2,3-dithiocyano-octane was prepared in three different methods. In the first, octene-2 was treated by method A and allowed to stand overnight in the ice box. Upon completion of method A the product separated as a yellow oil.

The second method was an exact duplication of the first except that the mixture was shaken on a machine for eight hours rather than allowed to stand in the ice box. The final product was a yellow oil.

In the third method small amounts of octene-2 were added to a solution of thiocyanogen (method B) until the brown color of the mixture disappeared. After filtration and evaporation the residue was dissolved in hot alcohol and filtered through Supercel. The filtrate was evaporated to 10 ml. and water added. The product separated as a yellow oil.

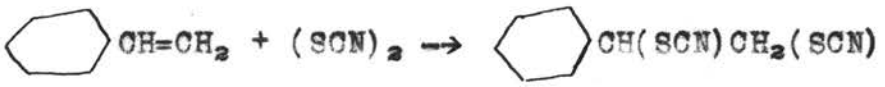
1,6-DIMETHYLHEXENE-3

The 1,6-dimethyl-3,4-dithiocyanohexane was prepared by method A slightly modified. The olefin was added to the sodium thiocyanate-acetic acid mixture and the copper sulfate was added in four portions at fifteen minute intervals.

During this time and for four hours after the last addition of copper sulfate, the mixture was shaken on a machine. Upon completion of method A the product separated as a yellow oil.

STYRENE

Styrene was treated by method A and allowed to stand in the ice box five hours. Upon completion of method A the 1-phenyl-1,2-dithiocyanoethane separated in fine, white crystals which were filtered off and purified by recrystallization from an alcohol-water mixture and dried in vacuum at room temperature, m. 102.5-103°. Analyzed for nitrogen and sulfur. Calculated for $C_8H_8(SCN)_2$; 12.72% N_2, 29.13% S. Found; 12.63% N_2, 28.87% S.



It is of interest to note that by using the same proceedure except that the mixture was left in the ice box overnight, a large amount of gas was formed in the flask and a yellow, crystalline product was obtained. No melting point determination or analysis was made.

d-LIMONENE

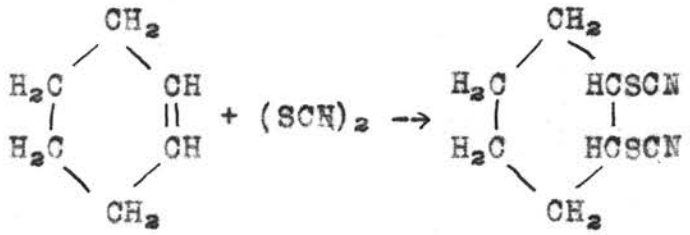
d-Limonene was treated by method A, shaken on a machine for six hours and divided into two portions. The first was allowed to stand in the ice box for three hours and the second for twenty-four hours. Upon completion of method A the limonene dithiocyanate separated as a yellow oil in both cases.

PINENE

Pinene was treated by method A and shaken for 20 minutes when the black color of the mixture disappeared. Upon completion of method A the pinene dithiocyanate separated as a brown oil.

CYCLOHEXENE

Cyclohexene was treated by method A and allowed to stand in the ice box overnight. Upon completion of method A the 1,2-dithiocyanocyclohexane separated in white crystals which were filtered off, purified by recrystallization from an alcohol-water mixture and dried in vacuum at room temperature, m. 58°-58.5°. Analyzed for sulfur. Calculated for $C_6H_{10}(SCN)_2$; 32.35% S. Found; 32.36% S.



3-METHYLCYCLOHEXENE-1

3-Methylcyclohexene-1 was treated by method A and the mixture shaken for four hours on a machine. Upon completion of method A the 1,2-dithiocyano-3-methylcyclohexane separated in white crystals which were filtered off, purified by recrystallization from an alcohol-water mixture and dried in vacuum at room temperature, m. 69.5°-70°. Analyzed for nitrogen. Calculated for $C_7H_{12}(SCN)_2$; 13.21% N_2. Found; 12.96% N_2.

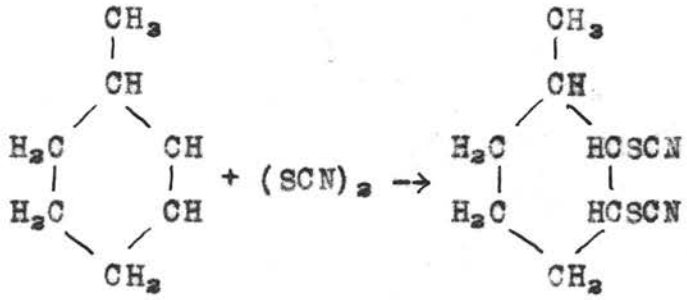


Table I gives a summary of the olefins investigated and the results as compared with the literature survey.

TABLE I

Properties of Olefin Dithiocyanates

Olefin	Found in Literature	Found by Experiment
Ethene	90° (8), (9), (10)	90°-90.5°
Propene	Oil (15)	103°-104°
Cyclopropane	33° (15)	Oil*
Allyl Alcohol	Oil (9)	Oil*
Allyl Bromide	None	Oil*
Butene-1	None	Oil*
Butene-2	None	Oil*
2-Methylpropene-1	Oil (15)	Oil*
Pentene-2	None	Oil*
1-Methylbutene-2	None	Oil*
Methyl Isoprene	130° (11)	120.5°-121°
Octene-2**	None	Oil*
1,6-Dimethyl hexene-3**	None	Oil*
Styrene	101° (8), (10) 101°-102° (9)	102.5°-103°
d-Limonene	None	Oil*
Pinene**	None	Oil*
Cyclohexene	None	58°-58.5°
3-Methylcyclohexene-1	None	69.5°-70°

*Remains an oil down to -10°.

**Commercial product. Probably a mixture.

DISCUSSION OF RESULTS

The table of results shows that the primary object of this research--to use thiocyanogen for making derivatives of olefins--was not realized as fully as was hoped for. Of the 18 olefins tested, only six were found to give solid dithiocyanates. The properties of the dithiocyanates of ethene and styrene were in agreement with those reported in previous investigations. Methyl isoprene dithiocyanate was found to have a melting point nine degrees lower than the literature value. The sharp melting point is indicative of a pure compound. However, no statement may be made as to the reliability of the value determined since no analysis to prove the purity was carried out because of the poor yield. Propene dithiocyanate was found to be a solid whereas a previous investigation reported it to be an oil. The dithiocyanates of allyl alcohol and 2-methylpropene-1 were found to be oils in agreement with results obtained by previous investigators. The dithiocyanate of cyclopropane was found to be an oil in contrast to the solid dithiocyanate reported in a previous investigation. It is of interest to speculate as to whether the cyclopropane-thiocyanogen reaction is one of ring substitution or of ring cleavage. In view of the reactions of cyclopropane with the heavier halogens and hydrogen halides it is probably the latter.

The dibromide of octene-1 was on hand but was not used on account of the improbability of its giving a solid dithiocyanate.

It may be noted that the olefins most likely to yield solid compounds with thiocyanogen are those of low molecular weight, those which are more highly unsaturated, and those which are substituted with aromatic groups.

Among the olefins recommended for future study might be listed the other two isomeric methylcyclohexenes and other members of the same homologous series, phenylated olefins like 1-phenylpropene-1, 1,1- and 1,2-diphenylethene, p-tolylethene and others, 1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and all olefins with multiple double bonds.

A very interesting extension of this work would be the application of selenocyanogen to the identification of olefins which would, in all probability, give derivatives of higher melting points (15).

All the solid compounds possess a characteristic, faintly disagreeable odor. It should be pointed out that, in any work of the type carried out in this problem, caution should be exercised as the thiocyanogen and the organic dithiocyanates are very painful skin irritants.

SUMMARY

The action of thiocyanogen on olefins was used to obtain olefin dithiocyanates suitable for use as derivatives in qualitative organic analysis.

Ethene dithiocyanate and styrene dithiocyanate were prepared and found to agree closely in melting points with earlier preparations.

The dithiocyanate of methyl isoprene was prepared and found to have a melting point nine degrees below that found in an earlier investigation.

Propene was found to give a solid dithiocyanate instead of an oil as previously reported.

Cyclohexene and 3-methylcyclohexene-1 gave solid dithiocyanates which have not hitherto been described.

Allyl alcohol and 2-methylpropene-1 gave dithiocyanates which were liquid, in agreement with earlier results.

Cyclopropane gave a liquid dithiocyanate instead of the solid obtained by an earlier investigator.

Allyl bromide, butene-1, butene-2, pentene-2, 1-methylbutene-2, octene-2, 1,6-dimethylhexene-3, d-limonene, and pinene gave liquid dithiocyanates which have not been mentioned in the literature.

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AUTOBIOGRAPHY

I, George A. Dysinger, was born on a farm southwest of Clayton, New Mexico, March 25, 1914. I attended the public schools of Hooker, Oklahoma, graduating from Hooker High School in May, 1932. I attended Panhandle Agricultural and Mechanical College, Goodwell, Oklahoma, from September, 1933, to August, 1936, the last year of which I worked as student chemist in the Panhandle Agricultural Experiment Station laboratory. I entered Oklahoma Agricultural and Mechanical College in September, 1936, where I worked as student chemist in the Agricultural Chemistry Research laboratory. I was graduated in June, 1937, receiving the degree of Bachelor of Science.

I entered the Graduate School of the Oklahoma and Mechanical College in September, 1937, and expect to receive my degree of Master of Science in June, 1938.

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Dorothy Swan

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